AN-1802-10

Rapid Determination of Pu in Steel Samples

Summary of Method Plutonium is separated and measured from 1-2 gram steel samples. Samples are digested with concentrated nitric, hydrochloric, and hydrofluoric acids. The digestate is evaporated to dryness, the residue dissolved in HNO_3/H_3BO_3, and a CaF_2/LaF_3 precipitate is used to concentrate the Pu and remove matrix. An optional NaOH fusion may also be performed, post sample digestion, to dissolve concrete or stone included in the sample and deal more rigorously with refractory Pu. Plutonium is separated from matrix impurities and potentially interfering radionuclides in the sample using 2 mL cartridges of Eichrom TEVA Resin. Plutonium is measured by alpha spectrometry following rare earth fluoride microprecipitation onto Eichrom Resolve filters. The chemical recovery of Pu, determined by ^{242}Pu tracer, was 90–99%. Measured values of Pu typically agreed to within 7-8% of reference values for 16 hour count times. The minimum detectable activity for Pu in 2 g samples with 16 hour count times was 0.25 mBq/g. A single operator can prepare batches of 12 samples for the measurement of Pu in less than 8 hours.

Reagents

TEVA Resin, 2 mL Cartridges (Eichrom TE-R50-S)
Nitric Acid (70%)
Hydrochloric Acid (37%)
Hydrofluoric Acid (49%) or Ammonium Bifluoride
Lanthanum Carrier (10 mg/mL)
Cerium Carrier (10 mg/mL)
Deionized Water
1.25M $Ca(NO_3)_2$
2M $Al(NO_3)_3$
^{242}Pu Tracer
Boric acid
$NaNO_2$
Ascorbic Acid
30% H_2O_2
10-20% (w:w) $TiCl_3$ in HCl
3.2M $(NH_4)_2HPO_4$*
Sodium Hydroxide*

Equipment

Vacuum Pump
Centrifuge
Muffle Furnace*
Hot Plate
Analytical Balance
Teflon Beakers (Zr Crucibles*)
50 mL and 250 mL Centrifuge Tubes
Alpha Spectrometry System
Vacuum Box (Eichrom AR-24-BOX or AR-12-BOX)
Cartridge Reservoir, 20 mL (Eichrom AR-200-RV20)
Inner Support Tubes-PE (Eichrom AR-1000-TUBE-PE)
Yellow Outer Tips (Eichrom AR-1000-OT)
Resolve Filters in Funnel (Eichrom RF-DF25-25PP01)

Figure 1. Sample Preparation

Add 1-2 g steel sample to Teflon beaker*.
*If using optional fusion, omit HF/H_3BO_3 and use Zr crucible.

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Add ^{242}Pu tracer, 5 mL 70% HNO_3, 20 mL 37% HCl, and 5 mL 49% HF. Digest on Hotplate to dryness.

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Add 1 mL 70% HNO_3, 10 mL 37% HCl, and 1 mL 49% HF. Digest on Hotplate to dryness.

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Add 5 mL 3M HNO_3-0.25M H_3BO_3 and 5 mL 37% HCl. Digest on Hotplate to dryness.

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Add 25 mL 1M HCl. Warm to dissolve. Transfer to 250 mL centrifuge tube. Repeat 2 additional times.

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Dilute to 170 mL with 0.01M HCl. Add 2 mL 1.25M $Ca(NO3)_2$,5 mg La, and 3 mL 20% $TiCl_3$.

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Add 25 mL 49% HF. Mix Well. Allow to sit 20 min. Centrifuge. Discard supernate.

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Dissolve precipitate in 7 mL 3M HNO_3-0.25M H_3BO_3, 6 mL 8M HNO_3, 7 mL 2M $Al(NO_3)_3$. Mix. Warm if necessary. Centrifuge. Check for solids.

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Continue to Pu Separation.

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Optional NaOH Fusion. Add 15-20 g NaOH. Fuse at 600C for 20 min.

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Dissolve in DI water. Transfer to 250 mL c-tube. Dilute to 100 mL. Add 2 mL 1.25M $Ca(NO_3)_2$, 5 mg La, and 8.5 mL 3.2 M $(NH_4)_2HPO_4$.

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Centrifuge. Decant supernate. Dissolve ppt. in 80 mL 1.5M HCl.

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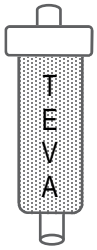
Figure 2. Load Solution Preparation and Plutonium Separation

(1) Ensure samples are cooled to room temperature.

(2) Add 1.25 mL of 1.5M ascorbic acid. Mix well. Wait 5-10 minutes.

(3) Add 1 mL of 3M $NaNO_2$. Mix well. Wait 5-10 minutes.

(4) Precondition 2 mL TEVA Resin with 5 mL 3M HNO_3.



(6) Load sample.

(7) Rinse sample tube with 5 mL 8M HNO_3 + 50 µL 30% H_2O_2.

(8) Add tube rinse to TEVA Resin.

(9) Rinse TEVA Resin sequentially with:
- 15 mL 3M HNO_3 (U decon.)
- 20 mL 9M HCl (Th)
- 5 mL 3M HNO_3

(10) Dispose of (4) to (9) as waste.

(11) Strip Pu with 15 mL 0.1M HCl-0.05M HF-0.01M $TiCl_3$.*

*If preparing alpha sources by electrodeposition, replace $TiCl_3$ with Rongalite or hydroxylamine.

(12) Add 50 ug Ce carrier and 0.5 mL 30% H_2O_2 to all samples. Mix well.

(13) Add 1 mL 49% HF. Mix well. Wait 15-20 minutes.

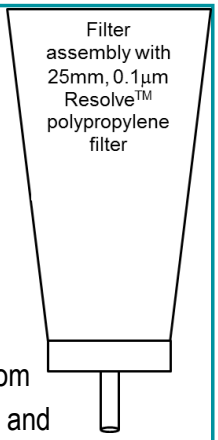
(14) Set up Resolve® Filter Funnel on vacuum box.

(15) Wet filter with 3 mL 80% ethanol followed by 3 mL DI water.

(16) Filter sample.

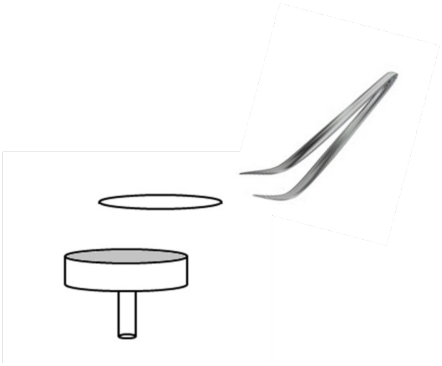
(17) Rinse sample tube with 5 mL DI water and add to filter.

(18) Rinse filter funnel with 3 mL DI water and 2 mL 100% ethanol.



(19) Draw vacuum until filter is dry.

(20) Remove filter from funnel assembly and mount filter on stainless steel planchet with 2-sided tape.



(21) Dry filter under heat lamp for 3-5 minutes.

(22) Measure actinides by alpha spectrometry.

Method Performance for Pu in Steel Samples

Details	Sample replicates	Reference (mBq/sample)	Measured (mBq/sample)	Average % Diff.	242Pu tracer % Yield
238Pu in 2 g Steel	5	37.0	37.7 ± 1.6	4.2	89.3 ± 2.3
239Pu in 2 g Steel	5	24.5	24.4 ± 1.6	6.6	96.5 ± 3.4
239Pu (refractory) in 2 g Steel	5	24.5	23.4 ± 0.9	3.8	98.9 ± 6.6
239 Pu in 5 g Steel	4	37.0	38.3 ± 1.0	2.6	92 ± 14

References

1) Sherrod L. Maxwell, Brian K. Culligan, Jay B. Hutchison, Robin. C. Utsey, Ralf Sudowe, Daniel R. McAlister, "Rapid method to determine plutonium isotopes in steel samples," *J. Radioanal. Nucl. Chem., 314(2), 1103-1111* (2017).